



New Understanding of High Temperature Corrosion Protection

Role of Sulfur and Reactive Metals Elucidated

An LBNL team led by Peggy Hou has developed new techniques to determine the chemical composition of the oxide/metal interface that develops on the surface as materials corrode. This interface plays a critical role in blocking further corrosion; thus the importance of understanding its characteristics. The new techniques have been used to clarify the mechanisms by which some elements (e.g. sulfur) weaken this interface and others (e.g. zirconium, yttrium, etc.) strengthen it.

All metal components operating at elevated temperatures rely on the growth of a surface oxide or "scale" for corrosion protection. A stable and adherent oxide scale provides maximum protection and the precise chemical composition of the interface has a large effect on its strength. For example, at high temperatures, sulfur, a common impurity in commercial high temperature alloys, can diffuse (segregate) to the oxide/alloy interface, where it weakens that interface. It is also known that the addition to the alloy of certain reactive metals such as zirconium and yttrium inhibits sulfur segregation, thereby maintaining the strength (and the corrosion protection) of the oxide layer. However, the details of this process are not well understood; the buried nature of the oxide/metal interface makes precise chemical characterization difficult.

The LBNL team developed a new method to study the metal/oxide interface. After producing protective scales by heating the alloys in dry oxygen at 900-1000 °C, the sample are transferred to an ultra high vacuum chamber. The oxide surface is then scratched with a diamond stylus. This causes spallation of the oxide scale, exposing the underlying alloy surface for chemical analysis with an Auger electron spectroscopy microprobe.

The new technique has been applied to scale formation of Fe₃Al, a prototypical high temperature intermetallic alloy. The protective scale formed on this alloy during high temperature oxidation is Al₂O₃, aluminum oxide. The team first studied commercially available Fe₃Al, which contains 28 ppm sulfur. In agreement with the current understanding of the role of sulfur, after a few hours of high temperature oxidation, up to 0.4 monolayers of sulfur had segregated at the interface, and the interface strength was a relatively low 4 J/m². The team then reduced the sulfur content of the alloy to less than 0.5 ppm by annealing the alloy in hydrogen before forming the oxide scale. In this case, there was no detectable sulfur at the interface and the interface strength was increased to 20 J/m². The team then studied an alloy with 25 ppm sulfur and 0.1 wt. % zirconium, a reactive metal. The results were surprising. As in the case of the alloy annealed in hydrogen, no sulfur was found at the interface, confirming that reactive metals serve to prevent sulfur from segregating to the interface to weaken it. However, the measured interfacial strength was >1000 J/m², substantially higher than in either of the two other cases. Thus the reactive metal has a strengthening effect at the interface beyond protecting it from sulfur contamination. High sensitivity chemical analysis of a cross section of the interface performed by the Corrosion Science and Technology Group at ORNL (one of LBNL's partners in the DOE Materials Science Center for Excellence corrosion project) revealed that zirconium is enriched at the scale/alloy interface. This implies that the reactive metal strengthens the interface by segregating between the aluminum oxide and the substrate. The mechanism by which the strengthening effect occurs is unknown, and is under investigation.

These experiments constitute the first detailed observations of sulfur and reactive metal kinetics and chemistry at growing oxide/alloy interfaces. The results could allow the fabrication of chemically designed interfaces that are highly resistant to high-temperature corrosion process.

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